A CALORIMETER FOR DETERMINING THE HEATS OF REACTION AT HIGH TEMPERATURES

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THESIS

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ABSTRACT

Apparatus.—A vacuum calorimeter containing an insulated platinum resistance furnace is described for use in determining reaction heats, and the heat absorbed in raising the temperature of a material in the furnace from room temperature to 1200°C, and also the heat evolved in cooling down the material from 1200°.

Materials experimented with.—Four typical clays are employed, namely A-1 English china clay, North Carolina kaolin, Tennessee ball clay No. 5, and Laclede-Christy raw flint clay. The calorimeter is calibrated with pure quartz.

Results.—The numerical data obtained are assembled in Table IV. The quantity of heat absorbed per gram per degree on heating the air dried clays over the complete temperature range 25–1200° amounts to 0.50–0.55 calories, whereas the heat evolved on cooling the final products per gram per degree through the range 1200–700° is 0.23–0.29 calories.

The heat absorbed in the ranges 24–420°, 420–900°, and 900–1200°, together with the heat evolved in the ranges 1200–900°, and 900–700°, are also given for all of the above clays.

I. Introduction

1. **Purpose of the Investigation.**—When refractory materials are fired, heat is absorbed, the net quantity depending upon the specific heats and upon the heats of reaction resulting from chemical and physical changes in the constitution of the fired material. Exothermic reactions help to raise the temperature of the materials whereas endothermic reactions require an additional amount of heat to complete them, before the temperature can again rise. In materials like clays, and in bodies containing them, these reactions are quite often not reversible, meaning that the heat absorption on firing is not equivalent to the heat evolution on cooling. It is impossible then, with such materials to obtain the heat absorption on firing by the method of mixtures, which is the usual method employed for determining specific heats.

In the method of mixtures, the substance is heated to a high temperature, and the resulting heated material is dropped into a calorimeter, and the heat evolved by the material measured by the increase in temperature of the calorimeter bath. The present investigation has primarily for its purpose the measurement of the heat energy required to raise the temperature of raw clays, from room temperature to 1200°C, by a method and apparatus devised for the work. An experiment is run continuously on one sample to the highest temperature, and the heat absorption is measured

for three separate ranges of temperature; then the energy source is cut off, and the heat evolved by the fired material as it cools to 700° is measured over two ranges of temperature.

All temperatures given in this paper are in degrees centigrade.

2. Data in Literature on Specific Heats of Minerals, Refractories and Clays.—These are all data on materials experimented with by the method of mixtures.

(*a*) *Minerals.* White[1] obtained the Interval Mean Specific Heats on the silica minerals, quartz and cristobalite, on the feldspars, anorthite, andesine, albite, microcline, and on other natural minerals as pseudo-wollastonite, and on some of the natural forms of magnesium silicate. White also worked with some of the glasses of the above materials. His range of temperature was from room temperature to 1400°. From the data, he calculated the true instantaneous specific heats at different temperatures. His data will be referred to later.

Wietzel[2] found the Interval Mean Specific Heats of cristobalite, quartz, chalcedony and silica glass up to 1400°. The data on quartz and cristobalite are discussed in a later chapter.

(*b*) *Refractories.* Bradshaw and Emery[3] have obtained the Interval Mean Specific Heats on some refractory materials up to 1400°. Table I gives their results in calories per gram from $t°$ to 25°.

TABLE I

INTERVAL MEAN SPECIFIC HEATS OF REFRACTORY MATERIALS $t°$ TO 25°

$t°$	Silica brick	Fire brick	Pure zirconia	Stourbridge fire brick
600	0.226–8	0.228	0.137	0.227
1000	.263–2	.265	.157	.263
1200	.282–3	.284	.167	.262
1400	.293–5	.297	.175	...

Tadokoro[4] experimented with different types of brick to 900°. The Interval Mean Specific Heats in calories per gram from $t°$ to 30° are given in Table II.

Moore[5] worked with a terra cotta body that had been burned to 1100°. In cooling from $t°$ to 0°, when $t°$ is equivalent to 500°, 700° and 900°, the Interval Mean Specific Heats in calories per gram are 0.235, 0.245 and 0.249, respectively.

[1] W. P. White, *Amer. Jour. Sci.*, **47**, 1–43 (1919).

[2] Rudolf Wietzel, *Z. anorg. allgem. Chemie*, **116**, 80 (1921).

[3] L. Bradshaw and W. Emery, *Trans. Ceram. Soc.* (Eng.), **19**, 84–92 (1919–20).

[4] Yoshiaki Tadokoro, *Sci. Repts.* (Tôhoku Imp. Univ.), **10**, 339–410 (1921).

[5] J. K. Moore, "Tests on the Thermal Conductivity of Terra Cotta Fireproofing," Thesis for B.S. Univ. Ill. (1908).

TABLE II

INTERVAL MEAN SPECIFIC HEATS OF BRICK, $t°$ TO 30°

$t°$	Magnesia	Red clay	Silica	Chrome	Shamotte
218	0.223	0.207	0.199	0.178	0.197
303	.238	.221	.218	.195	.209
382	.254	.239	.233	.210	.222
480	.263	.247	.246	.216	.238
579	.266	.249	.249	.221	.251
687	.265	.247	.250	.219	.255
796	.264	.242	.247	.218	.249
894	.263	.237	.242	.215	.241

(*c*) *Clays.* Knote[1] determined the specific heat of a flint clay from Olive Hill, Kentucky, from 150° to 22°. The raw clay had a specific heat of 0.237, the clay burned to 650°, a specific heat of 0.204, and when burned to 1050°, a specific heat of 0.200.

3. Method, General Description.—The method employed consisted of immersing in a thermostat at room temperature a small vacuum jacketed furnace containing the sample of material to be investigated. The furnace was heated electrically by means of a platinum heating coil and the energy supplied in this way was accurately measured by means of a recording wattmeter. A thermocouple was inserted in the center of the charge for reading its temperature. The whole furnace was encased in a nickel cylinder which was evacuated, the whole being immersed in the water of the stirred bath.

During the passage of the heating current, some of the energy supplied to the furnace leaked out through the nickel containing cylinder into the water of the bath. This tended to raise its temperature above that of the room. In order to prevent this and to measure the energy which leaked out in this way, ice water was admitted to the bath at such a rate as to keep its temperature practically constant. An equivalent amount of water from the bath overflowed and was collected in a container for weighing. When, with a given heating current, the temperature of the center of the charge became constant and remained so for some time, this temperature was read and the container which received the overflowing water was removed and replaced by a second container. The heating current was then immediately raised to the second level and the above procedure repeated, as soon as the temperature of the center of the charge had again become constant at the higher value.

By weighing the water which overflowed from the water bath, the amount of energy which leaked out of the furnace through each stage could be accurately computed. From the record of the wattmeter, the amount of energy sent into the furnace could be similarly accurately

[1] J. M. Knote, *Trans. Amer. Ceram. Soc.*, **14**, 394–8 (1912).

computed. The difference between these two amounts obviously represents the heat absorbed by the charge and the furnace parts. The heat was measured with an accuracy of about 1% in the present investigation.

In order to determine the amount of heat absorbed by the furnace parts during the operation, the same series of experiments was repeated, using in place of the charge of clay a charge consisting of a known weight of quartz whose specific heat curve up to high temperatures has been accurately determined. In this second series of experiments, the heat absorbed by the charge is known and by subtracting this from the total heat absorbed by the furnace plus the charge, the heat taken up by the furnace parts could be computed. By combining this value with the results obtained when using the various clays in the furnace, the heats absorbed by the clays themselves can obviously be calculated. It is estimated that this heat was measured with an accuracy of about 10%.

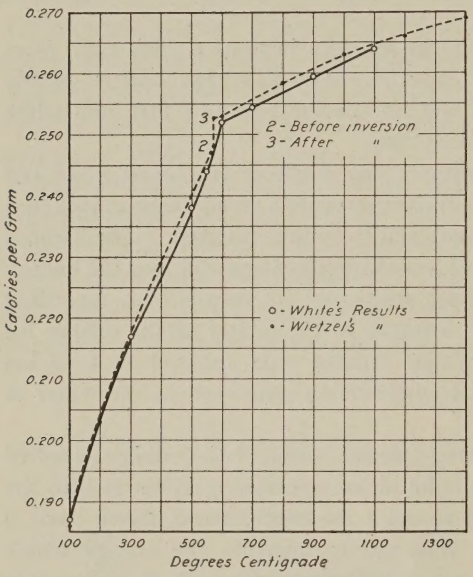

FIG. 1.—Average specific heats between 0° and t° of quartz.

It was found expedient to limit the temperature ranges to approximately 24–420°, 420–900°, 900–1200° for ascending temperatures, and 1200–900°, 900–700° for descending temperatures.

4. Available Specific Heat Data for Calibrating the Calorimeter.—The only data that are given on pure materials and over the complete range of temperatures from 0° to 1400° are those furnished by the experiments of White[1] and Wietzel.[2] The list of materials contains feldspars and magnesium silicates, which however are difficult to obtain with theoretical compositions. The glasses of these minerals crystallize fairly easily, which decreases their value for calibration purposes. The only other materials that can be considered are, then, quartz and cristobalite, data being furnished by both experimenters. Figures 1 and 2 give the complete data.

It will be noticed that the data on the quartz are much more concordant than are the data on the cristobalite. Wietzel has shown, as have others,

[1] W. P. White, *loc. cit.*

[2] Rudolf Wietzel, *loc. cit.*

as Washburn and Navias,[1] that the physical properties of cristobalite depend on the previous history of the material, that is, of preparation and of the extent of calcination.

For quartz, White gives values only up to 1100°, whereas Wietzel gives them as high as 1400°. In a preliminary run of the present investigation, crushed quartz heated to 1400°, in eight hours, gave inversion to cristobalite of about one quarter of the material. In two regular runs, quartz heated to 1200°, in ten hours each, gave no trace of inversion. This was determined by measuring the index of refraction of the grains. As the maximum temperature to be attained safely in the calorimeter is 1200°, quartz may be used to advantage. By adding Wietzel's result at 1200° to those of White's at lower temperatures, the data are complete for application to the present problem. As the work of White has extended over many years and with concordant results, preference has been given to his work.

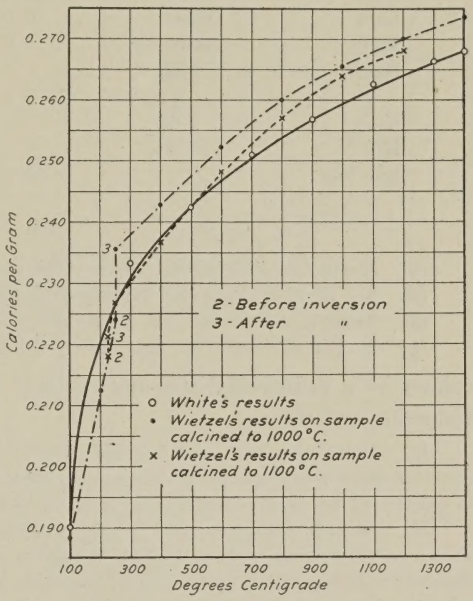

FIG. 2.—Average specific heats between 0° and t° of cristobalite.

II. Heats of Reaction of Clays at High Temperatures

5. Clays Experimented with.—The clays experimented with are typical of the different kinds used in the industries. Unfortunately the choice had to be limited to the purest clays, on account of the conditions under which the experiments were made. Attempts to experiment with brick clays and the like, have resulted in wrecking of the furnace, due to the bloating of the clays. The chemical analyses of the clays are given in Table III.

6. Reactions in Clays Due to Heating.—Mellor and Holdcroft,[2] working with kaolinite, determined from their time-temperature curves ob-

[1] Edward W. Washburn and Louis Navias, *Jour. Amer. Ceram. Soc.*, **5**, 565–85 (1922).

[2] J. W. Mellor and A. D. Holdcroft, *Trans. Ceram. Soc.* (Eng.), **10**, 94–120 (1910–11).

TABLE III

CHEMICAL ANALYSES OF THE CLAYS EXPERIMENTED WITH

	(1) Per cent	(2) Per cent	(3) Per cent	(4) Per cent
SiO_2	45.20	45.2	45.60	43.70
Al_2O_3	38.45	38.8	35.90	39.38
Fe_2O_3	0.45	0.3	1.00	0.79
TiO_2	trace	trace	1.00	1.95
CaO	trace	0.9	0.10	0.10
MgO	trace	.8	.30	.37
Na_2O	0.00	2.1	.46	trace
K_2O	.65		.72	
H_2O	14.80	...	...	....
Ign. loss	...	12.5	14.60	14.08
	99.55	100.6	99.68	100.37

(1) North Carolina kaolin (Harris Clay Co., Sprucepine).
(2) A-1 English china clay (Hammill and Gillespie).
(3) Tennessee ball clay No. 5 (Mandle Clay Mining Co.).
(4) Laclede-Christy raw flint clay (Missouri).

tained by a differential thermal method and from other experiments the following results:

(1) Just above 500°, heat is absorbed by an endothermic decomposition of kaolinite into free silica, free alumina and water. Graphically the "latent heat of decomposition" is calculated to be 42 calories per gram of raw clay.

(2) At approximately 800°, in the heating curve, there is an exothermic change shown corresponding with a physical change of the free alumina, whereby the alumina becomes less soluble in acids, less hygroscopic and more dense. The "latent heat of transformation" is determined graphically to have the value of 21.5 calories per gram.

(3) The formation of sillimanite in kaolinite when heated over 1200° is due to the recombination of the free alumina with some free silica formed at about 500°.

Wallach,[1] by a differential thermal method, has shown that kaolin, clays, mica and glauconite absorb heat when dehydrated between 450° and 600°, and evolve heat between 900° and 1000°. According to Le Chatelier the evolution of heat is due to a transformation of the alumina. Wohlin[2] substantiates the above results by a similar method. In clays, between 560° and 580°, there is an endothermic reaction, at 960° the reaction is exothermic. Bauxite, $Al_2O_3.H_2O$, has an endothermic reaction at 540°, while bauxite $Al_2O_3.3H_2O$ has an endothermic reaction at 310°—both having exothermic reactions at 1060°.

Zoellner[3] heated clays to high temperatures and then disintegrated the products in hydrofluoric acid. The residue consisted of sillimanite crystals. He determined that cone 10 (ca. 1300°) had to be reached before

[1] Ruby Wallach, *Compt. rend.*, **157**, 48–50 (1913).
[2] R. Wohlin, *Sprech.*, **46**, 719–21, 733–5, 749–51, 767–9, 780–2 (1913).
[3] Zoellner, *Brit. Clayworker*, **22**, 40 (1913).

sillimanite could be obtained, and also that the plastic clays gave only 3–5% sillimanite, whereas the lean clays (kaolins) gave 25% under similar conditions of firing.

In Fig. 3 is shown the results of a thermal analysis of North Carolina kaolin, determined from the time-temperature readings taken on heating a sample of the clay in a resistance furnace. It shows that most of the water of combination is disengaged between 535° and 600°.

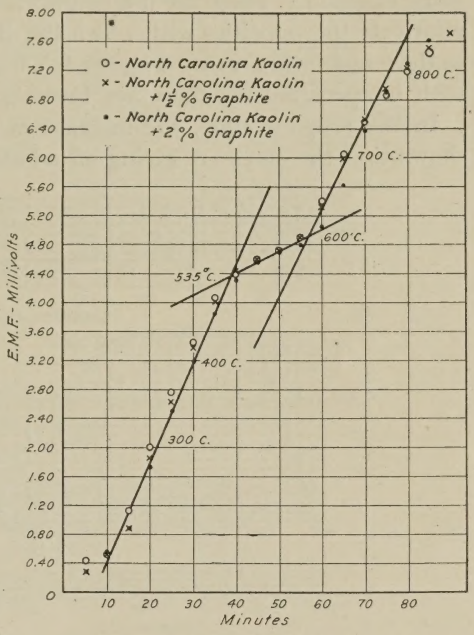

FIG. 3.—Thermal analysis of North Carolina kaolin.

Satoh[1] has determined qualitatively, by a very sensitive differential method, using quartz sand as a comparison substance, the heat reactions occurring in a Japanese kaolinite. His results may be summarized as follows

(1) Heat absorption up to 100°, due to evaporation of moisture contained in the specimen.

(2) Weak heat evolution from 100° to 300°, possibly due to oxidation of foreign minerals and organic substances.

(3) Heat absorption from 450° to 650°, due to the dehydration of the kaolinite.

(4) Heat absorption from 650° to 700°, due to the dissociation of kaolinite into free alumina and free silica.

(5) Weak heat evolution near 950°, due to the polymerization of the alumina.

(6) Weak heat evolution between 1200° and 1300°, due to the formation of amorphous sillimanite by the recombination of dissociated free alumina and free silica.

7. Evacuation of Raw Clays.—In preliminary runs the platinum container was filled with the powdered clay, and then evacuated in the system. Under these conditions, even with perfect control of the rate of evacuation, it was uncertain whether the clay had remained in the container, or had been partly expelled by the sudden expansion of gases. It was then found necessary to mold and press the clay, as described elsewhere, in order to keep the clay in the container. This procedure has a number of recommendations apart from the above-mentioned one. It approaches the methods used in practice, and also allows a larger sample to be employed—roughly from 200 to 300 grams.

[1] S. Satoh, *Jour. Amer. Ceram. Soc.*, **4**, 182–94 (1921).

8. Pressures Developed by the Dissociation of Clays.—Throughout the experiments, the vacuum pump is kept running, and with unhydrated materials, the pressure is kept down to a fraction of a mm. of mercury throughout the run. With clays, as the temperature varies, and with continuous withdrawal of the water vapor by the pump, a pressure is developed in the calorimeter depending upon the quantities of water vapor being expelled. These are not equilibrium vapor pressures, but they show relatively the velocities with which the dissociation of the clay takes place, as the temperature rises. Figures 4, 5, 6 and 7 show the changes in pressure with temperature for the clays investigated.

In the range 0–400°, the increase in pressure between 30° and 100°, shows that the clays are giving off adsorbed moisture held so tenaciously

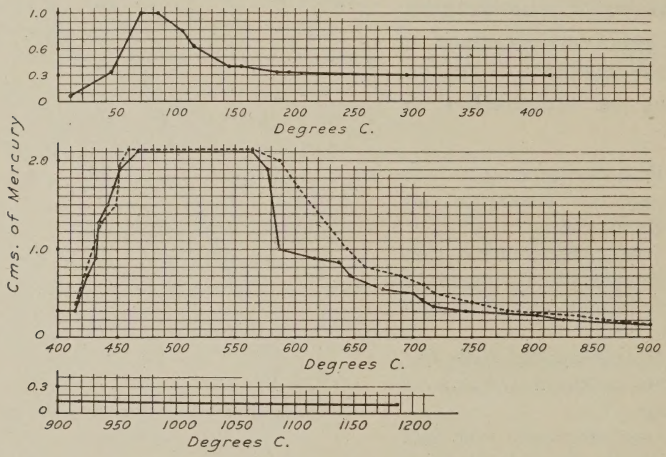

FIG. 4.—Pressure developed by the dissociation of North Carolina kaolin.

as not to be given off by the clays on drying at 110° at atmospheric pressure, or by continued evacuation at room temperatures.

In the range 400–900°, the dehydration of the clays seems to take place in two stages. In the first stage, the evolution of water vapor starts rapidly at about 475°, developing a pressure of about 2.2 centimeters. This maximum is maintained while the temperature rises 100–200°, depending upon the clay. Then appears the second stage, in which the dehydration velocity is suddenly lessened, but falls in a rather decisive and continuous manner, while the temperature rises 200–300° depending upon the clay.

In the range 900–1200°, only those clays containing organic matter developed pressures. The Laclede-Christy raw flint clay showed only a slight increase in pressure, but the Tennessee ball clay No. 5 developed

a rather high pressure. The run on the latter clay through the ranges 400–900°, and 900–1200°, was characterized by extremely bad odors issuing from the vacuum pump, due to the decomposition of the organic matter

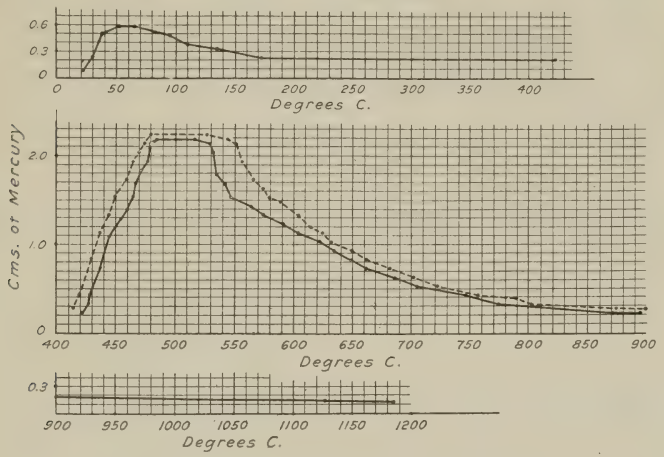

FIG. 5.—Pressure developed by the dissociation of A-I English china clay.

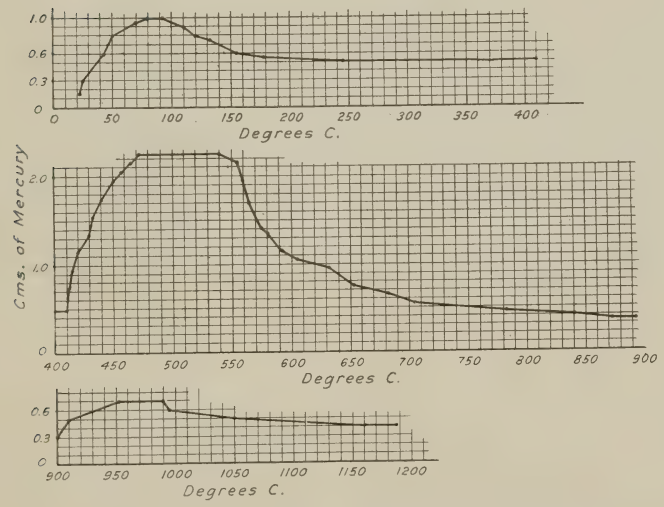

FIG. 6.—Pressure developed by the dissociation of Tennessee ball clay No. 5.

present. After cooling, the clay was found to be colored black throughout.

9. The Heat Effect of Carbon and Sulphur in Clays.—The combustion of one gram of carbon to carbon dioxide liberates 8080 calories of heat.

The combustion of one gram of sulphur to sulphur dioxide liberates 2240 calories. If the clay contains an appreciable amount of these constituents, especially of the former, the heat effect is theoretically large.

From the "Paving Brick Clays of Illinois,"[1] the following are the carbon and sulphur contents of some usable clays:—

	K_1	K_3	K_4	K_5	K_7	K_{14}	K_{15}	F_1	Average
S in %	0.27	0.16	0.14	0.11	0.13	0.24	0.25	0.32	0.18
C in %	1.44	1.50	.72	1.26	.71	1.01	.90	.92	1.05

Assuming these averages for a clay, the heat given up by the complete combustion of the carbon and sulphur in 100 grams of clay would be:

For C	$1.05 \times 8080 =$	8484 calories
For S	$0.18 \times 2240 =$	403 calories
		8887 calories

Assuming the specific heat of clay to be 0.70 in the range of combustion, 400–900°, then if heat was evolved at one time, and if all of the heat went to raising the temperature of the clay, the sudden rise of temperature would be about 125°. In practice, since the oxidation period extends over a long length of time, and over a wide range of temperature, such sudden increases in temperature are not to be expected. The heat evolved, however, is taken up by the material and its surroundings.

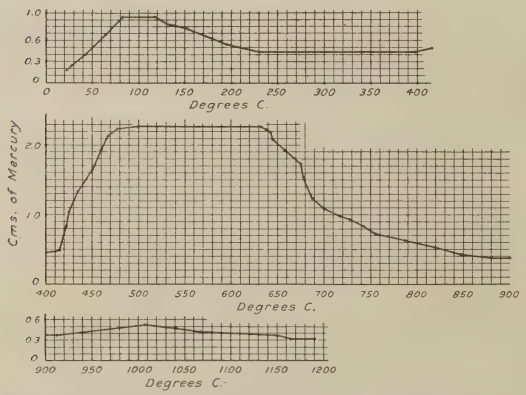

Fig. 7.—Pressure developed by the dissociation of Laclede-Christy raw-flint clay.

While obtaining the thermal analysis of the North Carolina kaolin an attempt was made to obtain a heat effect with the addition of 1.5% graphite, and in another case with 2% coal. The attempts were unsuccessful because these materials burned only partially, and also because the heat generated went to heating the furnace as well as the clay.

In the vacuum furnace there is no opportunity for the carbon and sulphur to oxidize and burn, hence these heat effects are lost. It is for this reason also that pure clays were selected.

[1] Ill. State Geol. Surv., *Bull.* 9, 284–5 (1908).

III. Description of Apparatus

10. General Set Up.—The following is a detailed description with dimensions of the apparatus. Fig. 8 is a photograph of the apparatus ready for a run. The letters correspond with those in the figures.

(*a*) *Ice Water Tank.* A wooden barrel 32 inches deep and 20 inches in diameter, heavily lagged on bottom and sides with felt.

(*b*) *Tube Stirrer.* A rotating metal spiral in a copper cylinder 36 inches long and 5 inches in diameter.

(*c*) *Needle Valve.* A $^1/_4$-inch brass globe valve, set between the ice

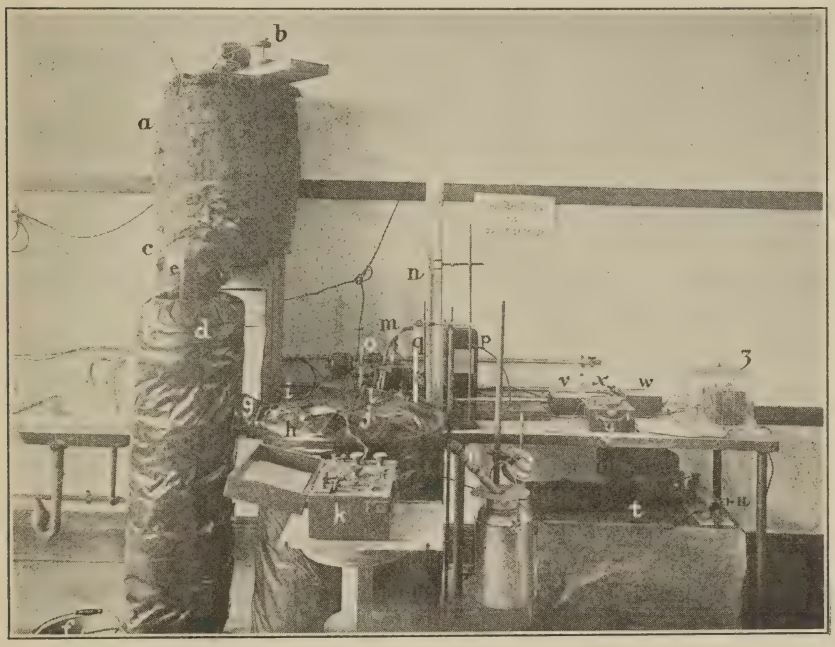

FIG. 8.—General view of apparatus.

water tank and the tube water cooler. With the valve wide open and ice water passing through the coils, the capacity is about 1000 cubic centimeters per minute.

(*d*) *Tube Water Cooler.* A galvanized iron cylinder, 48 inches high, 10 inches in diameter, containing the copper coils, with false perforated bottom, and with 1-inch outlet at bottom.

Copper Coils. Two coils, about 50 feet each, and $^3/_8$-inch and $^1/_2$-inch in diameter, respectively. They are coiled in a close spiral 6 inches in diameter and for a depth of 30 inches. They are con-

nected at the inflow end with a copper box into which the ice water flows from the ice water tank. At the outflow end there is an overflow box, made of copper, 3 inches deep and 3 inches in diameter, with the water level at $1^1/_2$ inches. The top of overflow box is 10 inches below the top of the galvanized cylinder, and the box has a copper tube extending out of it, to hold the long range zero-degree thermometer.

(*e*) *Thermometer, 0°, Long Range.* Mercury bulb, $1^1/_4$ inches long, mercury thread 16 inches long to 0° mark. Graduated in $^1/_{10}$° divisions from 0° to 10°. Stem $^1/_4$-inch in diameter. Immersed in water in box to depth of $1^1/_2$ inches. It was compared with a standard in ice water, and found to be exact at 0°.

(*f*) *Drainage Outlet.* The outlet for drippings from the ice water in the tube water cooler.

(*g*) *Vacuum Tube.* A tube 12 inches long and $^1/_2$-inch inside diameter was sealed at the ends onto a tube of $^3/_4$-inch inside diameter, leaving an air space between them. This space was evacuated to .002 millimeters pressure of mercury, and sealed off. The tube connects the overflow box, through the wall of the galvanized cylinder, to the calorimeter bath, through a hole in its side. The tube is heavily lagged with felt and covered with oilcloth.

(*h*) *Calorimeter Bath.* An enameled iron bath, 33 inches high and 22 inches in diameter. It is $29^1/_2$ inches deep from the overflow. With the calorimeter in place, the bath will hold 400 pounds of water, at 17°. It is lagged with 2-inch felt on sides and bottom, and stands on a wooden platform 5 inches above the floor. The felt is covered with oilcloth to prevent it from getting wet.

Bath Cover. This is a galvanized iron cover that fits tightly, and is covered with a 2-inch layer of felt. Soldered metal tubes in the cover allow for the extension of the stirrer shaft, Beckmann thermometer, electric current leads and vacuum connection.

(*i*) *Tube-Stirrer.* A rotating metal spiral in a copper cylinder 28 inches long and 3 inches in diameter. The stirrer is fastened to the side of the bath, and rotates so as to draw the water downwards in the tube.

(*j*) *Electric Current Leads.* Three pairs of wires emerge from a central tube in the cover. (1) Heavy wires for the current, (2) light wires for the potential leads, and (3) light wires for the thermocouple leads.

(*k*) *Potentiometer.* A Leeds and Northrup instrument with millivolt scale graduated in $^1/_{10}$ millivolts. The one hundredths can easily be estimated. The two graphs seen next to the instrument are (1) the e. m. f. temperature conversion chart, and (2) the deviation curve for the thermocouple.

(*l*) *Vacuum Connection.* A rubber hose connection from the calorimeter in the bath, through a tube in the cover, and connected on the outside of the bath to a glass double *L*. The double *L* then connects to (1) Vacuum pump, (2) mercury *U*-manometer and (3) stopcock leading directly to the atmosphere.

(*m*) *Vacuum Pump.* A Hyvac pump made by the Central Scientific Company. The pump is kept running continuously throughout an experiment.

(*n*) *Mercury U-Manometer.* The long arm was evacuated and sealed off. When attached to the evacuated apparatus, the mercury in both arms is at the same level.

(*o*) *Stopcock and Pinchcock.* A well ground stopcock with a pinchcock on a heavy rubber hose, to control the pressure in the vacuum furnace when necessary.

(*p*) *McLeod Gauge.* Capable of reading to one thousandth of a millimeter of mercury. The gauge is connected to the vacuum pump through one arm of a *T*, the other arm being connected to the double *L*.

(*q*) *Beckmann Thermometer.* Graduated in one hundredths of a degree. The bulb $1^1/_8$ inches long and $^1/_2$-inch in diameter rests in the water in the bath, a few inches away from the overflow.

(*r*) *Overflow (Bath).* As ice water is put into the bath through (*g*), the overflow of the bath escapes through (*r*).

(*s*) *Tared Container.* Cans with close fitting covers are used to collect the bath overflow.

(*t*) *Rheostats.* Two plate rheostats in series. A slide wire rheostat in parallel with one plate rheostat for fine adjustment.

(*u*) *Knife Switch.*

(*v*) *Ammeter.* 0–10 ampere range. Divisions, 0, 1, 2, from 2–10 in one-tenths.

(*w*) *Ammeter.* 0–50 ampere range. Divisions, 0, 5, 10, from 10–50 in $^1/_2$ units.

(*x*) *Knife Switch.*

(*y*) *Wattmeter.* General Electric Company. Scale 0–500 watts. Amperes 10 and 20, volts 75 and 150, maximum combinations.

(*z*) *Test Meter.* Portable Type IB-5, for alternating current circuits. Amperes 1 and 10. Volts 110. Cycles 60. Two coils, for 1 ampere fuse and for 10 ampere maximum through instrument. The instrument is a revolution counter with three dials.

Dial (1) reading total of 100 revolutions, divided in 10's.

Dial (2) reading total of 10 revolutions, divided in units.

Dial (3) reading total of 1 revolution, divided in $^1/_{100}$ revolution.

When using the 10 ampere coil on the 110 volt circuit, but irrespective of the voltage drop on it, the constant for the instrument

is 0.6 watthours per revolution. Maximum load, 10 amperes. General Electric Company product.

11. **Calorimeter Set Up. (Description of Figure 9.)**—(*a*) *Platinum Container.* Made of 0.004 inch sheet, $8^1/_4$ inches high, $1^3/_8$ inches in diameter, with the bottom end closed, weighing 51.0 grams.

(*b*) *Alundum Furnace Core.* 10 inches long, $1^1/_2$ inches bore, $^1/_8$-inch wall, closed at one end. It has a double thread for holding the resistance wire in place—$^1/_6$-inch apart.

(*c*) *Alundum Cylinder.* 10 inches long, $1^3/_4$ inches bore, and $^1/_8$-inch wall, open at both ends.

(*d*) *Porcelain Cylinder.* Made of a good refractory body, 11 inches high, 3 inch bore, and closed at one end.

(*e*) *Nickel Cylinder.* Made of sheet nickel, one millimeter thick, with a nickel sheet cap at the bottom. It is just large enough to hold the porcelain cylinder.

(*f*) *Porcelain Upper Support.* This is made to fit over the top of the nickel cylinder, $3^1/_4$ inches to $3^1/_2$ inches in diameter, ending in a hollow stem, $1^1/_8$ inches outside diameter and $1^1/_4$ inches high, which fits into the calorimeter cover.

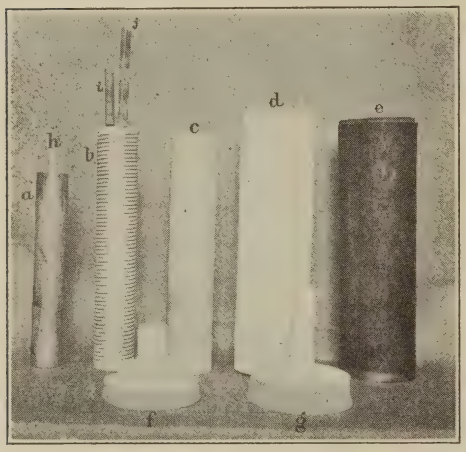

FIG. 9.—Platinum container and furnace parts.

(*g*) *Porcelain Lower Support.* This is made to hold up the nickel cylinder in a holder $3^1/_2$ inches in diameter, and 1 inch high, the holder terminating in a slightly tapered hollow stem 3 inches long and tapered from 1 inch to $^3/_4$-inch.

(*h*) *Porcelain Insulator.* About 6 inches long, 6 millimeter bore and 2 millimeter wall, closed at one end. It is imbedded in the material held in the platinum container, so that the closed end is situated half way down the material and centrally located.

(*i*) *Porcelain Insulator.* 6 millimeter bore and 2 millimeter wall.

(*j*) *Platinum Resistance Wire.* 28 feet long, 0.036 inch in diameter and weighing 120.30 grams, wound non-inductively on the core (*b*). Above the core, the ends of the wire are trebled so as to form heavy leads for the current, and are encased in the porcelain insulators.

Description of Figure 10.—(*a*) *Metal Calorimeter.* Made of nickel-plated copper, $14^3/_4$ inches high, $7^3/_4$ inches inside diameter, and $^1/_8$-inch wall. It has a bottom screwed in and soldered air tight. In the center of the bottom is soldered a hollow metal inset which holds the tapered end of the porcelain lower support in place.

(*b*) *Calorimeter Cover.* Made of nickel-plated iron. It slips onto (*a*) snugly to a depth of $^3/_4$ inch. Its center is cut out and threaded to take a $1^3/_8$ inch pipe.

(*c*) *Heavy Copper Leads.* These are connected to the platinum leads by means of nickel screw connectors.

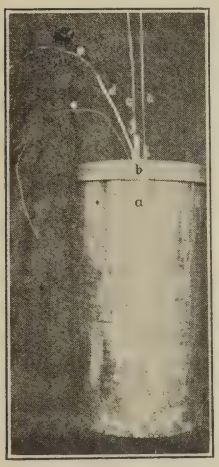

FIG. 10.—Metal calorimeter with furnace and thermocouple lead wires.

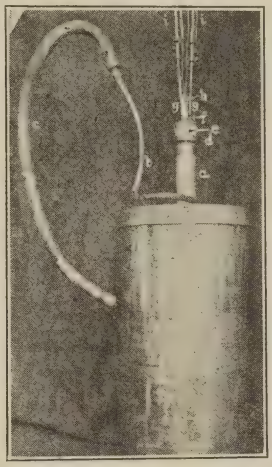

FIG. 11.—Metal calorimeter with cover stem showing excavating tube and partially insulated lead wires.

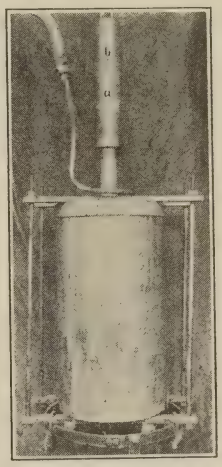

FIG. 12.—Calorimeter ready to be immersed in water bath.

(*d*) *Porcelain Insulators.* One millimeter bore and one millimeter wall.

(*e*) *Thermocouple.* Platinum, platinum-rhodium thermocouple, two feet long.

Description of Figure 11.—(*a*) *Cover Stem.* Made of nickel-plated copper, threads into calorimeter cover. It is $4^1/_4$ inches long and has a bore of $1^1/_8$ inches.

(*b*) *Copper Evacuating Tube.* Made of $^5/_{16}$-inch stock, and soldered into the cover stem about $^1/_4$-inch above the calorimeter cover.

(*c*) *Rubber Pressure Hose.* It connects the calorimeter to the vacuum pump, by way of the copper evacuating tube. It is coated with beeswax to make it air tight.

(*d*) *Threaded Collar.* Two inches in diameter, sweated onto the upper end of the cover stem.

(*e*) *Rubber Stopper.* This fits into top of cover stem.

(*f*) *Glass Tube Insulators.* These extend about 2 inches above the top of, and $^1/_2$-inch below the bottom of, the rubber stopper, and allow the heavy copper leads to pass through, and keep them apart for insulation purposes.

(*g*) *Heavy Copper Leads.* The same as shown in Fig. 10.

(*h*) *Porcelain Insulator.* Six millimeter bore and 2 millimeter wall. It passes through the rubber stopper and harbors the thermocouple, insulating it from the current lead wires. One wire of the thermocouple is strung with small bore porcelain insulators to insulate the two thermocouple wires from each other.

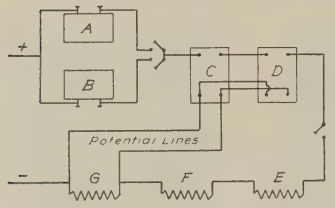

FIG. 13.—Electric wiring set up.

(*i*) *Current and Potential Leads.* To each heavy copper lead is attached, by means of a copper screw connector, two copper insulated leads, a heavy wire for the current, and a light wire, known as the potential lead wire, to be connected to the test meter.

Description of Figure 12.—(*a*) *Copper Extention Tube.* Copper Tube, $9^1/_4$ inches high and 2 inches in diameter that threads onto the collar of the cover stem. It is merely a protection for the wires from the surrounding water.

(*b*) *Water Level.* The water in the calorimeter bath reaches to level (*b*).

12. Electric Wiring Set Up. (Figure 13 Illustrates the Set Up.)—

(*A*) *Ammeter.* 0–10 ampere range.

(*B*) *Ammeter.* 0–50 ampere range.

(*C*) *Test Meter.* Revolution counter. Alternating current only.

(*D*) *Wattmeter.* Indicating wattmeter.

(*E*) *Rheostat.*

(*F*) *Rheostat.*

(*G*) *Electric Furnace.* Platinum wound furnace, operated on 110 volt alternating current circuit.

IV. Experimental Data Necessary for Calculating Specific Heats

In any range of temperature for which a run is made, the following data must be known:—

(1) The electrical energy expended in the resistance furnace.

(2) The heat absorption of the ice water used to counteract the rise in temperature of the bath.

(3) The temperature of the inflowing ice water.
(4) The temperature of the bath.
(5) The temperature of the material under investigation in the resistance furnace.

The following paragraphs describe the instruments used to obtain the above readings, and give their sensitivity and calibration, and all data and factors necessary for converting their readings to the purpose at hand.

13. Electrical Energy.—(*a*) *Portable Test Meter.* This instrument, of the induction coil type, is essentially a calibrated revolution counter. For the 10 ampere coil used in this work, the rating is 0.600 watthour per revolution, or 2160 watts per revolution. Allowing 4.186 watts to the calorie, gives the meter a value of 516.0 calories per revolution. The instrument was calibrated over its full range at 110 volts and found to be correct to better than 0.1%. At lower voltages and at the lowest wattages used in the experimental work, a comparison with an electrodynamometer type of wattmeter gave concordant results to within the accuracy of the comparison instrument of 0.1%.

(*b*) *Indicating Wattmeter.* It was found expedient to have an ordinary indicating wattmeter in the line, so that the wattage through the furnace could be seen at a glance, and easily controlled by means of the resistance in series with the furnace. A small amount of current is used in actuating the wattmeter, but as it is used in all runs for approximately the same wattages and for the same lengths of time, this correction is taken care of automatically.

14. Ice Water Heat Absorption.—(*a*) *Weighing the Overflow.* The run is started with the bath full and continuously stirred, and with the temperature of the bath constant. Ice water is allowed to flow in to keep the temperature of the bath constant, as heat is being transferred to the water from the calorimeter. The overflow is collected in cans, and for any range of temperature, the weight collected is equal to the weight of ice water delivered to the bath. The overflow is weighed to a gram.

Knowing the temperature of the ice water going into the bath, and the temperature of the overflow, the heat absorbed in this change in temperature is known. The total heat absorption of the ice water for the range of temperature can then be calculated.

Some of the ice water is utilized in counteracting the rise in temperature of the bath due to the heat caused by the friction of the stirrer in the bath.

(*b*) *Ice Water Correction for Stirring Friction.* After runs had been made on two days several months apart, the bath was allowed to be stirred for periods of four hours and the rise in temperature due to stirring noted. The increase in temperature amounted to 0.052° per hour.

On other occasions, the amounts of ice water necessary to lower the temperature of the bath 1°, were determined. In one case, 8442 grams

of ice water cooled the bath from 22.940° to 21.910°, with constant stirring for 30 minutes. As the raising of the temperature of the bath due to stirring is 0.026°, the true lowering of temperature of the bath is 22.940° + 0.026° — 21.910° = 1.056°. Hence at the average temperature of 22.425°, it requires 7994 grams of ice water to cool down the bath 1°. To counteract one hour of stirring at 22.425° requires 7994 × 0.052 = 416 grams of ice water.

At the average temperature of 27.587° it requires 6554 grams of ice water to cool down the bath 1°. At 27.587°, one hour of stirring will be counteracted by 341 grams of ice water. The ice water used in all experiments had a temperature of 0°.

By plotting these results the ice water stirring correction for any temperature of the bath can be found by inspection.

(*c*) *Heat Capacity of Water.* By means of an electrical continuous flow method, Callendar[1] and Barnes[2] have found the specific heat of water over the range of 0° to 100°. Callendar gives the variation of total heat h, with the temperature t, in the form of an equation that is of great value in the present work, for it is necessary to know the heat capacity of the ice water used to keep the temperature of the bath constant.

$$h - t = 1.1605 \log_{10}\left(\frac{t+20}{20}\right) - 1.1464\left(\frac{t}{100}\right) + 0.42\left(\frac{t}{100}\right)^2 + 0.30\left(\frac{t}{100}\right)^3$$

Thus the heat absorbed by one gram of ice water in changing its temperature from 0° to 23.560° amounts to 23.709 calories.

(*d*) *Heat Capacity of the Bath and Contents.* From preliminary experiments it was determined to be 180,440 calories.

15. Temperature of the Ice Water.—A long range mercury thermometer has its bulb in the overflow box of the tube water cooler. It measures the temperature of the ice water flowing into the calorimeter bath. The thermometer was compared with a French Standard, certified by the Bureau of Standards, and was found to be correct at 0°. There is no difficulty in having a continuous supply of ice water at 0°, with the arrangement used, provided constant attention is given to it.

16. Temperature of the Bath.—The temperature of the bath is read by means of a Beckmann thermometer graduated in hundredths of a degree, and calibrated against a thermometer recently certified by the Bureau of Standards. The bulb is situated near the overflow and measures its temperature. The temperature of the room is regulated so as to coincide with the temperature of the bath to within a few tenths of a degree.

[1] H. L. Callendar, *Proc. Roy. Soc.* (London), **86A**, 254–7 (1912).

[2] H. T. Barnes, *Trans. Roy. Soc.* (London), **199A**, 149–263 (1902).

17. Temperature of the Material in the Furnace.—The junction of a two-foot platinum, platinum-rhodium thermocouple is imbedded in the center of the material which is being heated in the furnace. The two ends of the couple extend one inch above the top of the cover of the calorimeter bath. They are connected to a Leeds and Northrup potentiometer by copper leads. A thermometer hanging just above the bath measures the cold junction temperature, which is corrected in the temperature measurements. The thermocouple and potentiometer were calibrated against the freezing points of pure metals supplied by the Bureau of Standards for such work, and the deviations in temperature were plotted as suggested by Adams.[1]

V. Heat Insulation

18. Furnace Insulation.—From preliminary work, it was found that the heat loss from the furnace had to be reduced as far as possible. The advantage in decreasing the input of electrical energy was in increasing the fraction of heat expended on the material. This was accomplished (*a*) by running the furnace under vacuum conditions instead of at atmospheric conditions, and (*b*) by packing the furnace core with a good insulating material. In order to reach 1100° under atmospheric conditions, about 750 watts from a 12–15 ampere current had to be expended, whereas with the present vacuum furnace, 350 watts from an 8-ampere current will give 1200°. The maximum current capacity of the test meter is 10 amperes.

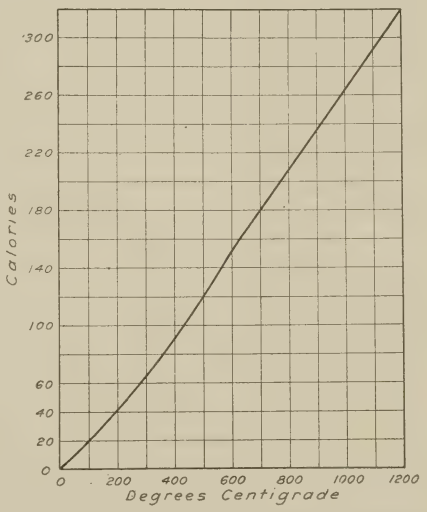

FIG. 14.—Heat capacity of 1 gram of quartz calculated from White's results.

It has been found that fused zirconia has the lowest specific heat (0–100°, 0.1075)[2] and heat conductivity (about 0.00039)[3] of any material suitable for furnace packing.

19. Bath Insulation.—The calorimeter bath is covered on its sides, top and bottom with two-inch felt to minimize heat exchange with the room. The temperature of the room was kept to within a few tenths of a degree of the temperature of the

[1] Leason H. Adams, "Symposium on Pyrometry," *Am. Inst. Mining Met. Eng.*, 165–78 (1920).

[2] J. W. Marden and M. N. Rich, Bur. Mines, *Bull.* **186,** 20 (1921).

[3] R. S. Hutton and J. R. Beard, *Proc. Faraday Soc.*, **1,** 266 (1905).

bath so as to minimize the radiation exchange. The felt is covered with oilcloth to prevent it from getting wet.

20. **Insulation for the Ice Water System.**—The ice water tank and the tube water cooler are covered on all sides with two-inch felt.

The valve and pipe connections between the ice water tank and the tube water cooler are very heavily covered with felt. The connection between the tube water cooler and the bath is a vacuum tube, which is also well covered with felt and oilcloth. The vacuum tube, set at an angle of 30°, is connected by rubber hose to the overflow box in the tube water cooler, and leads the ice water directly into the tube stirrer in the bath by means of another piece of rubber hose.

VI. Preparation for an Experiment

All of the parts of the apparatus mentioned in this chapter are described in Chapter II, and are illustrated in the figures accompanying it.

21. **Preparation of the Sample.**—If the material is inert like quartz, the crushed particles are filled into the platinum container. If the material is a clay, which is finely divided and contains water of combination, it must first be molded.

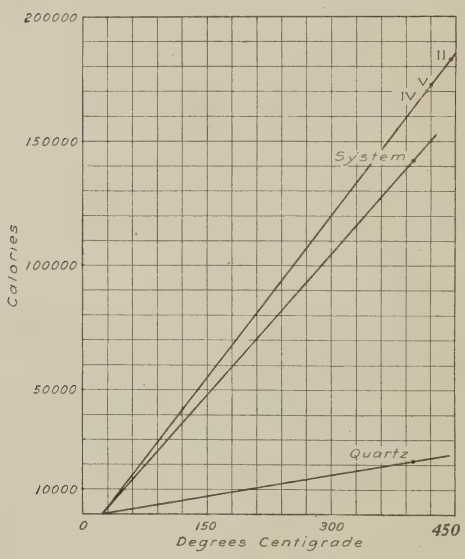

FIG. 15.—Quartz runs and heat capacity of system in range 23.560–420°C. Heat capacity of system 23.560– 00° = 142,400 calories.

The clay is made to pass a 20-mesh screen, and then worked with water until a plastic mass is obtained. The mass is then put into a screw press and forced through a $1^1/_2$-inch orifice. The stiff column is cut up into pieces 1 to 2 inches long. Half of these pieces are then centrally bored with a $^5/_{16}$-inch cork borer. All of the pieces are allowed to dry at 110° over night. The solid pieces with a total length of 4 inches are trimmed down to fit the platinum container snugly. The hollow pieces are trimmed down to fit the container, and are also hollowed out to allow the porcelain thermocouple protection tube to slide through them. The container is then filled up with these hollow sections, and the protection tube is slipped into place.

22. Assembling the Calorimeter.—The platinum container and its charge are then slipped into the furnace core, so that it stands on the false bottom consisting of a thin alundum disc resting on a porcelain ring. The furnace core is slipped into the alundum cylinder, which is surrounded by the zirconia packing, held in place by the porcelain cylinder, with the nickel cylinder on the outside. The weight of the furnace parts are:—

	Grams
Nickel and porcelain cylinders	1406.0
Zirconia packing	1321.0
Alundum cylinder	220.8
Alundum core	205.3
Platinum container	51.0

The nickel cylinder and contents are now ready to be set onto the porcelain bottom support which is in its holder in the base of the metal calorimeter. The porcelain upper support is now put on, and then the metal cover of the calorimeter is forced on.

The lead ends of the platinum resistance wire are now sheathed with the porcelain protection tubes, and are attached by nickel screw connectors to two bare heavy copper leads. The cover stem, provided with a roll of dehydrated mica that fits snugly on the inside, is then slipped over the copper lead wires and screwed into place, thereby holding the porcelain upper support in position by its extension below the cover.

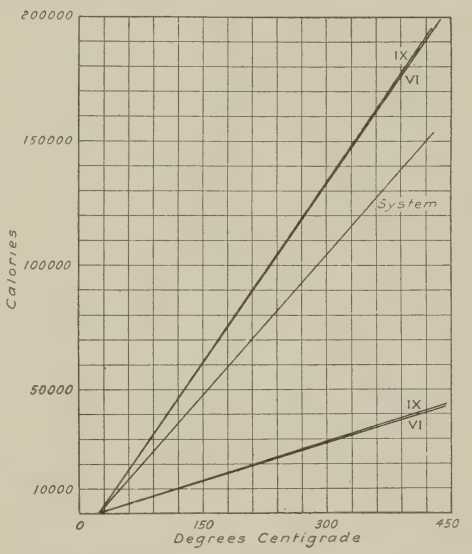

FIG. 16.—Heat capacity of A-I English china clay 247.5 grams in range 24–420°C. VI, 23.560–422° = 41,400 calories; IX, 23.560–415° = 41,000 calories.

A rubber stopper fitting into the cover stem carries in it two short glass tubes through which the heavy copper leads can just pass, and also carries a porcelain protection tube through which the thermocouple wires are led. When the rubber stopper is in place, its porcelain protection tube just touches the porcelain tube that is inserted in the material. The thermocouple is now inserted into place, its two wires being insulated from each other by small porcelain insulators. The copper lead wires are strung with glass tubing and are held in position so that there can be no short circuiting.

The two openings through which the lead wires enter the glass tubes in the stopper, and the openings whereby the thermocouple wires enter the porcelain protection tube, are now sealed with De Khotinsky cement. All other joints are made vacuum tight by painting them with a heavy layer of beeswax. To each heavy copper lead are attached by means of a copper screw connector, the two lengths of insulated copper wire. The screw connectors are insulated with rubber tape. The copper extension tube is now slipped over the four insulated lead wires and over the separately insulated thermocouple wires, and threaded into place. The joint is made water tight with a layer of beeswax. The apparatus is clamped into its metal frame and is ready for immersion in the bath.

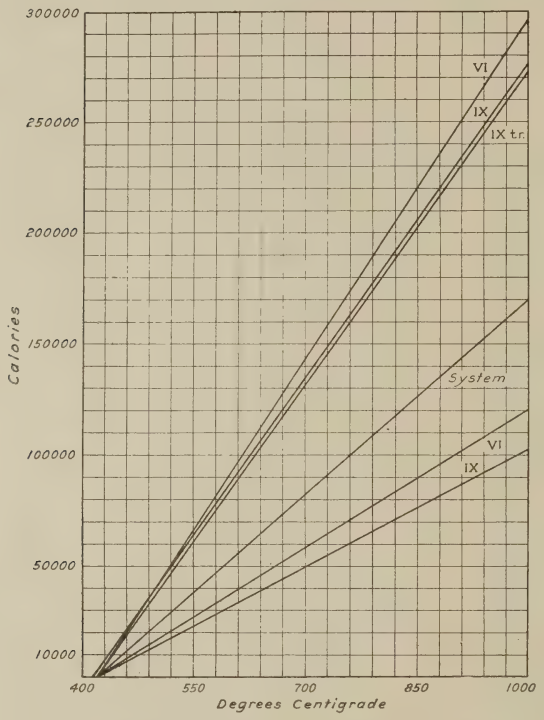

FIG. 17.—Heat capacity of A-I English china clay 247.5 grams range 400–900°. VI, 421–900° = 121,200 calories; IX, 421–900° = 103,200 calories.

23. Evacuating the Calorimeter.—The calorimeter bath is filled with water and the calorimeter set in the middle of it. The cover is put on so that the six wires from the calorimeter pass directly through the central tube. The rubber hose attached to the calorimeter is connected to the vacuum pump. The lead wires are connected to the source of current and the instruments, and the thermocouple wires are connected to the potentiometer.

The vacuum pump is started and the system is evacuated for several hours, to get rid of adsorbed air. The pressure is then usually below a millimeter. The pump is then shut off, and the system allowed to remain evacuated.

24. Ice Water Supply.—On the day before a run is to be made, the ice water tank is filled with water and crushed ice and stirred continuously. The tube water cooler is filled with crushed ice. From time to time the ice is shaken down and packed around the coil to insure intimate contact.

This process of packing and refilling is made every half hour during the run. The thermometer in the overflow box records the temperature of the ice water. During the run, the ice water tank is frequently supplied with water and ice, to keep the head of water on the valve constant. Usually about 600 lbs. of ice are sufficient for the complete run.

VII. Experimental Procedure

25. Ascending Temperatures.—When the calorimeter bath is stirred and filled just to overflowing, and the temperatures of the bath and room are the same, with the ice water supply at 0°, and the vacuum pump working smoothly, the test meter is read and a tarred can placed under the overflow. The current is turned on, and the resistance in the circuit varied to give the required wattage through the furnace. The wattage is continuously watched and kept constant, for from preliminary work it is known that this wattage will raise the furnace temperature the required amount.

The temperature of the bath is kept constant by varying the ice water flow into the bath. Normally the fluctuation of the temperature can be controlled to ±0.01°. The test meter readings are recorded. If the material being heated is a clay, the pressure developed in the furnace is recorded with the corresponding temperature of the clay. If the substance being heated is an inert material like quartz, a pressure in the calorimeter is artificially developed by working the pinchcock attached to the stopcock tube in one arm of the double L-tube in the vacuum system. The pressure curve followed is that of the clays at corresponding temperatures, thus making the heat insulation for the quartz run equivalent to the heat insulations found for the clay runs.

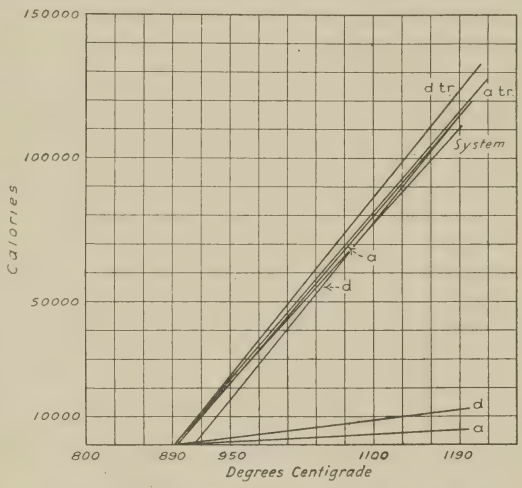

FIG. 18.—Heat capacity of A-I English china clay 216.2 grams in range 900–1200°C. IX, Ascending temp. (*a*) 892–1187° = 5,200 calories. Descending temp. (*d*) 1187–892° = 12,200 calories.

When equilibrium has been attained, that is when the furnace temperature has reached its maximum, the exchange of heat between the calorimeter and the ice water inflow is balanced. In practice, the equilibrium is considered to have been attained, when the rise in temperature of the

furnace, in the neighborhood of the maximum temperature, is even and very slow, in the order of $^1/_2°$ a minute. When this stage has been reached, the furnace temperature and test meter readings are recorded, and the overflow can replaced by an empty one, as soon as the temperature of the bath coincides with the initial temperature of the run. The wattage is then increased and the procedure repeated for the second range of the run.

The data obtained are then the total electrical energy consumed in the furnace, the total weight of ice water used, and the temperature to which the material has been heated. The weight of the material, the temperature of the ice water and of the bath, are already known. Similar data are found for each stage of the run.

With clays the main dehydration period exists between 420° and 900°, making it necessary to have this range all in one stage of the experiment. This then limits the run to three stages for the ascending temperatures. With 90–110 watts 420° can be reached in the furnace; then increasing to 200–240 watts will raise the temperature to 900°, and finally increasing to 300–350 watts, will give 1200° as the maximum temperature.

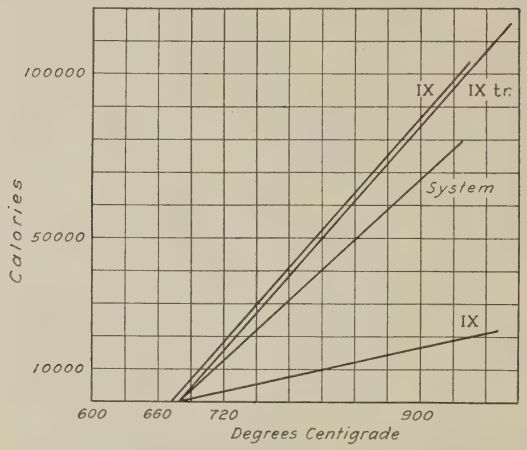

FIG. 19.—Heat capacity of A-I English china clay 216.2 grams in range 900–700°C. IX, 912–679° = 17,500 calories.

26. Descending Temperatures.—At the end of the last ascending temperature range, when equilibrium has been reached, the current is cut off, and the heat given up by the calorimeter to the bath is balanced by ice water. The temperature falls fast and continuously.

The descending run is divided into two stages, roughly 1200–900°, and 900–700°, the only data being obtained, are the quantities of ice water used for each descending range of temperature.

VIII. Heat Capacity of the "System"

27. Heat Capacity of Quartz.—The quartz used in the calibration runs was a Baker and Adamson product of crushed crystals, analyzing 99.98% SiO_2, and having indices of refraction 1.544–1.553, and a specific gravity of 2.654.

The heat capacity of the quartz was calculated from the results of White,[1] in Fig. 1, to give the values for one gram of quartz as represented graphically in Fig. 14. By plotting a similar curve for 251 grams of quartz, the weight used in the calibration runs, the heat capacity of the quartz between any two temperatures in the ranges 24–420°, 420–900°, 900–1200°, 1200–900°, and 900–700°, can be easily obtained and used for deriving the heat capacity of the "system."

28. Heat Capacity of the "System."—Several calibration runs were made with the quartz, and the net heat absorbed in raising the temperature of the quartz and the "system" through the ranges mentioned above were calculated from the data on electrical energy input, the quantity of ice water used to keep the temperature of the bath constant, and from the stirring-friction ice water correction. These results of the net heat absorbed, in all of the ranges of temperature for the calibration experiments, do not differ in duplicate runs by more than ±1%. The steps in the calculations are very similar to those made for the clays.

The net heat absorptions obtained in each temperature range are plotted with the calculated heat absorption for the quartz, an example being given in Fig. 15. The experimental data curves are marked with Roman numerals. In most cases the initial temperatures in the various ranges covered by the calibration runs and by the experimental clay runs are different, and for calculating purposes their corresponding curves have to be transposed parallel to themselves to pass through a common origin. Such transposed curves are marked "tr" on the figures. Where distinction has to be made between ascending and descending temperature curves, they are accordingly designated "a" and "d" on the figures.

By subtracting graphically the calculated heat absorption of the quartz from the heat absorption of the combined quartz and "system," determined experimentally, the heat capacity of the "system" is obtained, and its curve is marked accordingly.

These "system" curves are then used for obtaining the heat absorption of the clays, by subtracting them from the net heat absorption values, determined experimentally for the clays and the "system" in the requisite ranges of temperature. The resultant data are:

HEAT CAPACITY OF THE "SYSTEM"

Temperature range		Calories	Cal. per 1°
23.560–400°		142,400	379
421–900°		170,079	355
892–1187°	ascending and descending	109,778	372
892–679°		65,317	307

[1] W. P. White, *loc. cit.*

IX. Experimental Data for the Heat Absorbed and Evolved by Clays during Firing and Cooling

29. A-1 English China Clay.—The following are the detailed experimental data and the resulting calculations for duplicate runs VI and IX, made on 247.5 grams of air dried A-I English china clay:

(*a*) *Range 24–420°*

		Energy input		
Run	Temp. interval	Revolutions	Ice water, grams	Duration in hours
VI	23.560–422°	461.30	3,086	2.93
IX	23.560–415°	452.70	2,954	2.75

The net heat energy used is then obtained:

		Energy in calories		
Run	Temp. interval	Electrical	Ice water	Net
VI	23.560–422°	238,030	45,379	192,651
IX	23.560–415°	233,594	43,956	189,638

The net heat energy absorbed is represented in Fig. 16 as the upper curves marked VI and IX. The curve marked "system" is transposed from the quartz calibration curves. By subtracting the "system" curve from the upper curves, the lower curves are obtained, these representing the heat absorbed by the clay alone. Numerically the data are:

		Heat absorption in calories	
Run	Temp. interval	Total	Per gm. per deg.
VI	23.560–422°	41,400	0.420
IX	23.560–415°	41,000	0.423
			Av. 0.422 ± 0.002

(*b*) *Range 420–900°*

		Energy input		
Run	Temp. interval	Revolutions	Ice water, grams	Duration in hours
VI	422–894°	2748.00	50,956	8.33
IX	415–895°	2787.00	52,217	7.80

The net heat input is:

		Energy in calories		
Run	Temp. interval	Electrical	Ice water	Net
VI	422–894°	1,418,000	1,129,200	288,800
IX	415–895°	1,438,100	1,164,000	274,100

The curves for the net energies are given in Fig. 17. The net results differ from the average value by ±3%. The values for the heat absorbed are:

		Heat absorption in calories	
Run	Temp. interval	Total	Per gm. per deg.
VI	421–900°	121,200	1.022
IX	421–900°	103,200	0.871
			Av. 0.947 ± 0.075

(*c*) *Range 900–1200°*

Run	Temp. interval	Energy input: Revolutions	Energy input: Ice water, grams	Energy input: Duration in hours
VIa	894–1186°	774.82	12,606	1.42
IXa	895–1187°	897.53	15,402	1.68
IXd	1187–912°	....	5,025	0.55

These results may be summarized:

Run	Temp. interval	Energy in calories: Electrical	Energy in calories: Ice water	Energy in calories: Net
VIa	894–1186°	399,810	235,410	114,400
IXa	895–1187°	463,130	349,230	113,900
IXd	1187–912°	.....	113,920	113,920

The curves corresponding to the net energy consumption are given in Fig. 18.

Between 892° and 1186° the ascending curves VIa and IXa vary only by 500 calories in 115,000, or a difference of ±0.21%. On subtracting the heat absorption for the "system," the total heat absorptions for the clay differ by 500 calories, which now represents a difference of ±4.6%.

The weight of the dehydrated material in run VI was 216.8 grams and in run IX 216.2 grams corresponding to losses of weight of 12.40% and 12.65%, respectively. The heat absorption and evolution are calculated per gram of air dried clay, and per gram of dehydrated clay.

Run	Temp. interval	Heat absorption in calories: Total	Heat absorption in calories: Per gram air-dried clay per deg.	Heat absorption in calories: Per gram dehydrated clay per deg.
VIa	892–1186°	5,700	0.078	0.089
IXa	892–1187°	5,200	0.071	0.082
			Av. 0.075	0.086
			±0.004	±0.004
		Heat evolution in calories		
IXd	1187–892°	12,200	0.167	0.191

(*d*) *Range 900–700°*

Run	Temp. interval	Energy input ice water, grams	Duration in hours	Net heat in calories
IX	912–673°	4,136	0.75	90,948

The corresponding curve is given in Fig. 19:

Run	Temp. interval	Heat evolution in calories: Total	Heat evolution in calories: Per gram air dried clay per deg.	Heat evolution in calories: Per gram dehydrated clay per deg.
IX	912–679°	17,500	0.303	0.347

(*e*) *Average Heat Absorption and Heat Evolution*

To heat 1 gram of air-dried A-I English china clay from 25° to 1200° requires 644 calories.

Table IV

Heat Absorbed and Evolved by Clay during Firing and Cooling

(For the first two clays the values given are the average results of two independent experiments and the deviations from this average are indicated)

Clay type	Loss on ignition, per cent	Heat absorbed per gram per degree on heating the air-dried (110°) clay over the temperature ranges given				Heat evolved per degree on cooling the resulting quantity of fired clay			Specific heat of the fired clay cal./gm., 1200–700°	Dehydration period		
		25–420°	420–900°	900–1200°	25–1200°	1200–900°	900–700°	1200–700°		Pressure rises	Period of maximum pressure, 20 mm.	Pressure falls to 3 mm.
N. Car. Kaolin.....	14.0	0.49	0.69	0.23	0.50	0.23	0.28	0.24	0.28	25° to 460°	460° to 570°	570° to 780°
		±0.07	±0.05	±0.01	±0.035	±0.01	±0.06	±0.05	±0.05			
A-1 English China....	12.5	0.42	0.95	0.075	0.55	0.17	0.31	0.20	0.23	25° to 480°	480° to 540°	540° to 760°
		±0.01	±0.07	±0.004	±0.07							
Tenn. Ball No. 5.....	13.8	0.47	0.53	0.51	0.51	0.20	0.33	0.25	0.29	25° to 470°	470° to 550°	550° to 830°
Laclede-Christy Raw Flint.....	13.0	0.47	0.68	0.24	0.50	0.17	0.37	0.25	0.29	25° to 470°	470° to 630°	630° to 850°
Average.....		0.46			0.51	0.19	0.32	0.24	0.27			

Temp. interval	Calories
25–420°	395 × 0.422 × 1.00 = 167
420–900°	480 × 0.947 × 1.00 = 455
900–1200°	300 × 0.086 × 0.87 = 22
	Total 644

The average heat absorption per degree for A-I English china clay between 25° and 1200° is then 0.55 calories.

One gram of A-I English china clay, heated to 1200°, will evolve heat, on cooling, as follows:

Temp. interval	Calories
1200–900°	300 × 0.191 × 0.87 = 50
900–700°	200 × 0.347 × 0.87 = 60
	Total 110

or an average heat evolution of 0.22 calories per degree between 1200° and 700°.

30. Tennessee Ball Clay No. 5.—250.9 grams of air-dried clay were used, the results being given in Table IV. The heat absorbed in the ascending temperature range 900–1200° was large, part of the heat being absorbed by gaseous reactions. This assumption is substantiated by the gas pressure developed in the furnace, the foul smell of decomposed organic matter issuing from the vacuum pump, and the black appearance of the burned clay indicating organic matter.

31. North Carolina Kaolin.—Duplicate runs on 219.6 grams of clay were made, there being no unusual features to record.

32. Laclede-Christy Raw Flint Clay.—303.4 grams of clay were employed. A small gas pressure was developed in the ascending temperature range 900–1200°, probably explaining the increase in heat absorption as compared with the heat evolution in cooling over the same range of temperature.

X. Summary and Conclusions

The numerical results obtained are displayed in Table IV. They represent the data obtained for four types of clays.

33. Conclusions.—The following points and conclusions are brought out by the data presented in the table:

(1) All four clays contain approximately the same amount (14%) of moisture in the air dried condition.

(2) During the initial period of heating (up to 420°), in which all of the hygroscopic and some of the chemically combined water is driven out all of the clays absorb approximately the same amount of heat, 0.46 calories per gram per degree.

(3) Between 420° and 900° the remainder of the chemically combined water is driven out, most of it between 470° and 600°. During this period two of the clays, the North Carolina kaolin and the flint clay, show the same heat absorption, about 0.7 calorie per gram per degree. The other two clays behave differently, the English china absorbing 0.95 and the Tennessee ball only 0.53 calorie per gram per degree.

(4) During the final or finishing period 900° to 1200°, the North Carolina kaolin and the flint clay again exhibit similar behavior, each absorbing about 0.2 calorie per gram per degree. The English china clay, however, absorbs only 0.075 calorie per gram per degree over this range. Since this is less than the specific heat of the fired clay (0.17) in this temperature range, it shows that some reaction is taking place which evolves heat. Over the same range the Tennessee ball shows a heat absorption of 0.51 calorie per gram per degree and by a similar process of reasoning this clay is evidently undergoing some reaction which absorbs heat.

(5) Over the whole firing period all four clays behave alike as regards the total heat which they absorb during the firing operation, the heat absorption amounting to 0.5 calorie per gram per degree.

(6) Stated in another way, the amount of heat which must be put into the clay ware in order to completely fire it, if the finishing temperature is 1225° amounts to 1200 × 0.5 or 600 calories per gram of bone dry body.

(7) If, however, the heat content of the fired ware is utilized during cooling (as, for example, to heat the air for a drier) the net heat required by the various reactions which occur in the clay during the firing operation is 1200 × (0.51–0.24) or 320 calories per gram of bone dry body; or, stated in another way, 1 gram bone dry clay at 25° = 0.86 gram fire clay at 25° + 0.14 gram water vapor at 25°–320 calories.

(8) If we subtract from these 320 calories the heat required to vaporize the 0.14 gram of water present (*i. e.*, 77 calories), the remainder, about 240 calories, represents the heat absorbed by the dehydration reaction (at room temperature to produce liquid water) plus the net heat absorbed by all of the other chemical reactions which occur during the firing (also at room temperature).

(9) The results given above supply for the first time reliable data on the heat absorption of clay in a form suitable for use in heat-balance calculations.

(10) No attempt has as yet been made to correlate the above results with the burning behavior of these clays.

The results here presented of course apply strictly only to the four clays investigated. Moreover, they should be looked upon as the initial results in an entirely new field of investigation. They represent a new type of

calorimetric work and their principal value is the indication which they give of the possibilities in this field.

Incidentally it may be pointed out that the calorimetric method developed in connection with this investigation can be used to determine the heat effects of other high temperature processes such, for example, as the heat of fusion of a glass batch or the heat absorbed in manufacturing cement clinker.

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The following are the writer's publications:

"The Products of the Calcination of Flint and Chalcedony." Edward W. Washburn and Louis Navias. *Journal of the American Ceramic Society*. Vol. 5, p. 565–585, (1922).

"The Relation of Chalcedony to the other forms of Silica." Edward W. Washburn and Louis Navias. *Proceedings of the National Academy of Sciences*. Vol. 8, p. 1–5, (1922).

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